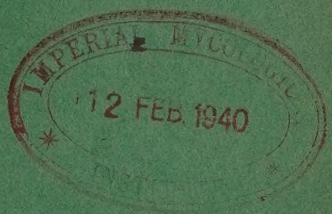
Vol. 9, Communications 241 (Rhodes & Fairfield Smith: The Viscosity of Preserved and Concentrated Latex, Part I)
& 242 (Rhodes: The Viscosity of Preserved and Concentrated Latex, Part II).

THE JOURNAL OF THE RUBBER RESEARCH INSTITUTE OF MALAYA



DECEMBER 1939

Published by
The Rubber Research Institute of Malaya
and printed by
Kyle, Palmer & Co., Ltd.,
Kuala Lumpur, F.M.S.

Edited by H. J. Page on behalf of the Board of the
Rubber Research Institute of Malaya.

THE VISCOSITY OF PRESERVED AND CONCENTRATED LATEX

PART I

RELATIONSHIP BETWEEN DRY RUBBER CONTENT AND VISCOSITY*

BY

EDGAR RHODES AND H. FAIRFIELD SMITH

Summary

Based on a large number of observations on preserved field latex and latex concentrates, mathematical expressions are derived for the viscosity-d.r.c. relationship over the d.r.c. range 0 to 68 per cent. It is demonstrated that the logarithm of viscosity is proportional to the tangent of d.r.c., and is approximately proportional to the ratio of rubber to serum. The observations have also been compared with theoretical equations put forward by Einstein, Guth, Bächle, Hatschek and Arrhenius. A viscosity table is presented which it is hoped may serve as a datum line for the viscosity of "average" latex.

Introduction

Data on the viscosity of preserved and concentrated latex are meagre, and in most cases results have not been reported in absolute values. In the present work a large number of observations on preserved field latex, centrifugal concentrates, and filtration concentrates have been made; and from them mathematical expressions have been derived which express with reasonable accuracy the viscosity of preserved latex and concentrates within the range of 0 to 68 per cent dry rubber (d.r.c.).

The first-named author has been responsible for the experimental work resulting in the data here presented; whilst the second-named author has been responsible for the analysis of the data, and for the derivation and interpretation of the mathematical expressions.

* The original paper under this title was published in *The India-Rubber Journal* January 7, 1939; the present paper is a revision.

Experimental

Preserved Field Latex

It is well known that different samples of preserved field latex of identical dry-rubber-content do not necessarily have identical viscosities. Differences are noted from source to source, and from time to time at the same source. It was sought to smooth out these variations, and obtain values for what might be termed average preserved latices, by making a large number of determinations on latex from different sources chosen to cover the widest possible range of dry-rubber-content for natural latex. Altogether, 950 samples of natural latex were collected, and tested after having been ammoniated with 26 per cent ammonia to an ammonia content of 0.5 per cent. The samples were collected as opportunity offered over a period of approximately six months from about twelve different sources, of which one, namely Kepong Estate, Selangor predominated. The latices of low dry-rubber-content (26 to 32 per cent) were of necessity obtained mainly from a single area of rubber which was being subjected to a mild form of "slaughter tapping" prior to replanting, while the rich latices (d.r.c. 44 to 52 per cent) came from a different area of the same estate during the first few days of normal tapping after rest.

Dry-rubber-content and viscosity determinations were carried out in duplicate on each sample. The first 533 samples were tested for viscosity in a simple pipette viscometer calibrated with solutions of cane sugar. The 417 samples collected subsequently were tested in a Höppler viscometer. All tests were at a temperature of about 30°C. The detailed results on the individual samples, together with the records of the source of each sample, were destroyed by fire at the Institute, but summary sheets escaped. These form Table I below. In making the summaries the results had been grouped into classes of 2 per cent dry-rubber-content, and the mean d.r.c. and mean viscosity had been calculated for each class. No other information remains. Observations obtained with the two viscometers are very similar.

Centrifugal Concentrates

Seventy-three samples of centrifugal concentrates were made available to us by the courtesy of Dunlop Plantations, Ltd. These were prepared to cover a range of dry-rubber-content of approximately 56 to 63 per cent. They were tested by the pipette method, under conditions similar to those for normal preserved latex. Here again details of the individual tests were lost by fire, but a summary showing the mean dry-rubber-content and mean viscosity

TABLE I

Preserved Field Latex

d.r.c. per cent	(a) Viscosity by Pipette apparatus			(b) Viscosity by Höppler Viscometer		
	No. of Samples	Mean d.r.c. per cent	Mean Viscosity centi-poises	No. of Samples	Mean d.r.c. per cent	Mean Viscosity centi-poises
> 24—26	3	25.2	3.5	—	—	—
> 26—28	16	27.4	3.2	10	27.4	3.2
> 28—30	118	29.3	3.7	33	29.3	3.7
> 30—32	106	30.9	4.1	44	31.2	4.2
> 32—34	30	32.9	4.7	83	33.2	4.8
> 34—36	34	35.1	5.6	63	35.0	5.4
> 36—38	33	37.3	5.6	70	36.9	5.9
> 38—40	61	39.4	6.3	51	38.8	6.4
> 40—42	92	40.9	7.2	28	40.8	7.2
> 42—44	25	42.8	8.6	12	42.8	8.3
> 44—46	7	45.0	9.8	8	45.1	9.8
> 46—48	3	47.5	14.2	8	46.8	11.0
> 48—50	6	48.9	14.2	6	49.1	13.1
> 50—52	2	50.2	16.0	1	50.4	14.2
Total	536			417		

by groups of 1 per cent d.r.c. escaped destruction, and forms Table II.

TABLE II

Centrifugal Concentrates

d.r.c. per cent	No. of Samples	Mean d.r.c. per cent	Mean Viscosity centipoises
> 56—57	3	56.6	27.7
> 57—58	3	57.8	31.8
> 58—59	10	58.6	38.1
> 59—60	21	59.6	40.5
> 60—61	31	60.4	45.1
> 61—62	4	61.3	48.5
> 62—63	1	62.9	57.5
Total	73		

CONCENTRATE-SERUM MIXTURES AND CONCENTRATE-SKIM MIXTURES

Determinations in the range provided by natural preserved latex and centrifugal concentrates do not give a complete picture of the relationship between dry-rubber-content and viscosity, and, in order to obtain more complete pictures, recourse was had to the preparation of concentrate-serum and concentrate-skim mixtures. Two procedures were used.

In the first, preserved field latex was filtered in a number of Leclanché cells, themselves placed in damp chambers to avoid evaporation concentration of the filtered serum. The filtered serum and the filtration concentrate were collected, and these, together with the original unconcentrated latex, provided a means of producing mixtures covering the whole range of 0 to 68 per cent dry rubber. Mixtures of the original latex with varying amounts of its concentrate were used for the high zone determinations, and similar mixtures of latex with its own filtered serum were used for the lower zone. For experimental purposes, concentrate-latex-serum mixtures were prepared for test from three different lots of latex. Two of the lots (Series 1 and Series 2, Table III)

came from the same estate on different days, and the third (Series 3 ,Table III) came from a different estate. Viscosity was measured by the Höppler instrument.

TABLE III

Serum-latex and Latex-filtration-concentrate Mixtures						Centrifugal Skim-cream Mixtures	
Series 1. Estate A		Series 2. Estate A		Series 3. Estate B		Series 4. Estate A	
d.r.c.	Viscosity centipoises	d.r.c.	Viscosity centipoises	d.r.c.	Viscosity centipoises	d.r.c.	Viscosity centipoises
0	1.08	0	1.01	0	1.06	10.4	1.40
4.6	1.32	3.6	1.16	3.2	1.19	15.2	1.70
8.8	1.43	7.1	1.38	6.7	1.37	20.3	2.02
10.5	1.59	9.9	1.45	9.4	1.52	24.9	2.60
13.1	1.64	12.9	1.69	12.1	1.81	26.0	2.75
14.5	1.68	16.0	1.84	15.3	1.96	27.2	2.95
17.2	1.89	19.0	2.07	17.7	2.06	28.9	3.10
18.7	2.04	22.0	2.33	20.2	2.36	31.0	3.60
19.5	2.10	25.3	2.66	23.5	2.65	31.9	3.85
20.6	2.25	28.2	3.05	26.9	3.26	33.5	4.20
21.9	2.38	31.3	3.62	29.6	3.80	34.3	4.30
25.3	2.65	34.2	4.30	32.7	4.35	35.9	4.82
27.5	2.96	34.9	4.73	36.5	5.99	36.7	5.00
29.7	3.27	37.3	5.63	38.2	6.19	37.7	5.48
30.2	3.46	39.3	6.00	40.0	6.68	38.9	5.80
34.8	4.74	41.3	6.56	41.7	7.91	40.1	6.40
35.9	5.02	43.2	7.43	43.8	9.16	41.3	6.85
38.0	5.62	44.5	8.40	46.1	11.50	42.2	7.3
39.8	6.12	47.7	11.59	47.8	12.81	43.8	8.3
42.2	6.95	49.5	12.48	49.7	14.89	45.0	9.2
44.9	9.08	51.6	14.22	51.7	18.38	45.2	9.7
47.1	10.93	52.6	15.93	53.7	22.05	45.8	11.0
49.1	12.27	53.8	19.63	56.0	28.74	47.7	12.4
50.5	13.78	55.3	21.56	58.0	39.18	49.1	13.2
52.5	16.62	57.0	26.64	59.6	49.62	50.1	14.2
54.1	19.69	59.0	31.85	62.1	72.30	51.2	15.5
55.9	23.7	59.7	32.48	62.6	79.84	53.3	18.8
57.2	32.9	61.1	40.13	64.8	111.4	55.6	24.5
59.1	41.2	61.9	46.5	66.4	186.8	57.3	28.5
60.9	51.9	62.8	52.0			59.0	37.2
61.8	56.7	64.8	75.5			60.7	49.1
66.2	159.5	65.4	100.5				
		67.5	153.1				

In the second procedure a batch of latex drawn from the same estate as Series 1 and 2 was centrifuged, and the centrifugal concentrate and skim so produced were used in preparing skim-cream mixtures, Series 4, covering the range 10 to 60 per cent dry rubber. These were tested by the pipette method.

Table III and Fig. 3 show the experimental results. The four series are very similar, the only difference of note being that whereas Series 3 falls in line with the observations on field samples, Series 1, 2 and 4 (all from the same estate) are consistently lower. It has been observed that latex from the latter estate is invariably less viscous than that from the estate which supplied the parent latex of Series 3.

Discussion

When tested at low rates of shear, latex, like other colloidal suspensions, may show varying coefficients of viscosity depending on the rate at which it is measured (Madge, 1935). In the following discussion we assume that our observations represent "limiting coefficients of viscosity." We make this assumption because results obtained with two different viscometers are very similar, and because there is no discontinuity at points where observations with the Höppler viscometer have been made with balls of different weights.

The main purpose of this work being merely to obtain descriptive data, no attempt has been made to investigate the theory of the subject. But in seeking an empirical formula by which the data may be conveniently described we have taken the opportunity to compare our observations with some of the equations which have been put forward.

Most theoretical work on the viscosity of suspensions starts from the work of Einstein. For very dilute suspensions of rigid spherical particles in a dispersion medium of equal density, he derived theoretically, from hydrodynamic considerations, the relationship.

$$\eta = \eta_0 (1 + 2.5\varphi)$$

where φ is the volume of disperse phase in unit volume of the dispersion, η is the viscosity of dispersion, and η_0 is the viscosity of the dispersion-medium.

Assuming that the relative specific gravity of the rubber phase is 0.910, and of serum is 1.022 (Fairfield Smith, 1939), and that the volume of the disperse phase is not increased over the volume of rubber by water of hydration and other adsorbed substances, we may put as estimates of φ in our data

$$\varphi = \frac{1.022\ w}{0.910 + 0.112\ w}$$

where w is the weight of rubber in unit weight of latex.

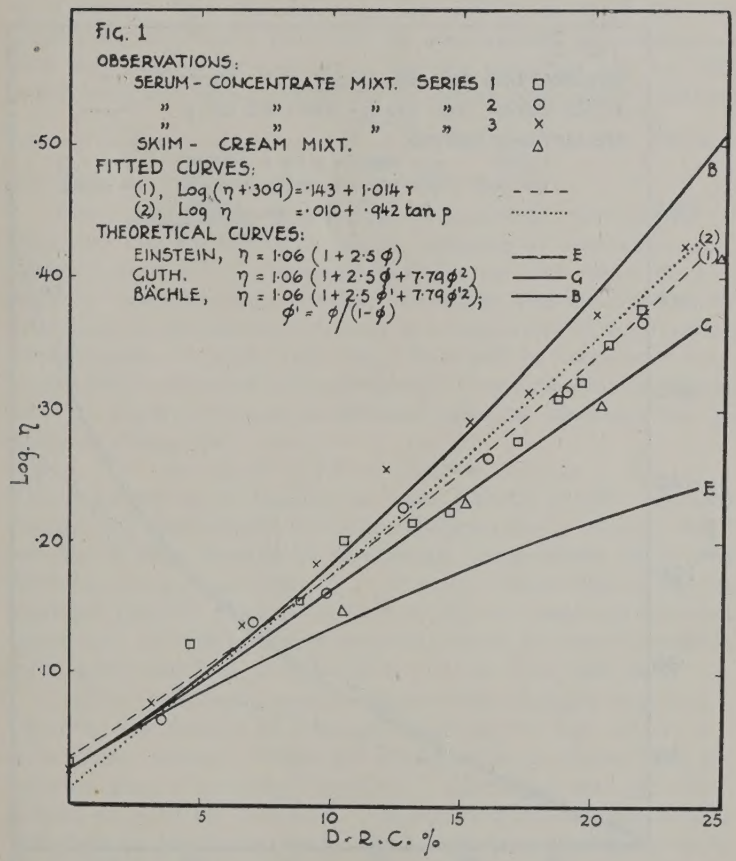


FIG. 1
OBSERVATIONS:
SERUM - CONCENTRATE MIXT. SERIES 1
" " " " 2
" " " " 3
SKIM - CREAM MIXT.
FITTED CURVES:
(1), Log (η + ·309) = ·143 + 1·014 τ
(2), Log η = ·010 + ·942 tan p
THEORETICAL CURVES:
EINSTEIN, η = 1·06 (1 + 2·5 φ)
GUTH. η = 1·06 (1 + 2·5 φ + 7·79 φ²)
BÄCHLE, η = 1·06 (1 + 2·5 φ' + 7·79 φ'²);
φ' = φ/(1 − φ)
E
G
B
·50
·40
·30
·20
·10
Log. η
5
10
15
20
25
D.R.C. %

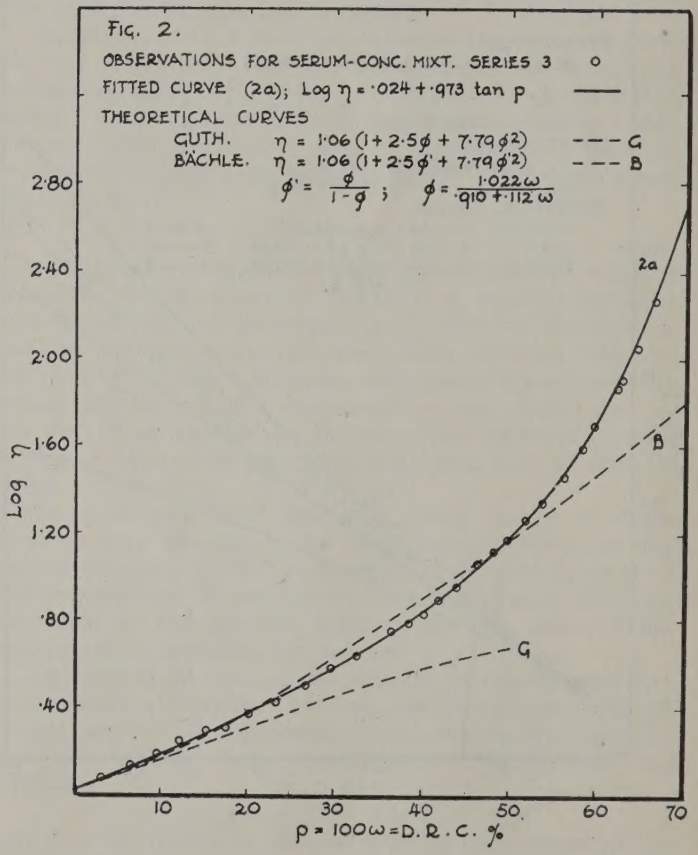


Fig. 2.
OBSERVATIONS FOR SERUM-CONC. MIXT. SERIES 3 o
FITTED CURVE (2a); Log η = ·024 + ·973 tan p
THEORETICAL CURVES
GUTH. η = 1·06 (1 + 2·5φ + 7·79φ²) --- G
BÄCHLE. η = 1·06 (1 + 2·5φ' + 7·79φ'²) --- B
φ' = φ/(1−φ) ; φ = 1·022ω/(·910 + ·112ω)
2a
B
G
Log η
2·80
2·40
2·00
1·60
1·20
·80
·40
10
20
30
40
50
60
70
p = 100ω = D.R.C. %

Figure 1 shows that the rate of change of viscosity with concentration in dilute suspensions of latex-serum mixtures is perhaps slightly greater than, but yet not dissimilar to, that predicted by Einstein's law. Our data are not suitable to determine this point accurately since there are no observations on suspensions with less than 3 per cent d.r.c.; but for equations (1) and (2), which have been fitted to the data for serum-concentrate mixtures (see p. 182), the values of $\frac{d(\eta - \eta_0)}{d\varphi}$, when $\varphi = 0$, are 2.68 and 3.37 respectively; Einstein's law predicts 2.5.

Guth and his co-workers have considered adjustments to Einstein's law for forces of inertia, influence of viscometer wall, mutual action of the suspended particles on each other, electroviscosity and Brownian motion. Of these the adjustment for interaction of the particles becomes most important with increasing concentration; it is the only one which will be considered here. Guth (1936) evaluated this adjustment as an expansion in powers of φ for which he has so far obtained only the coefficient for the quadratic term, *viz.*

$$\eta = \eta_0 (1 + 2.5\varphi + 7.79\varphi^2 + ...)$$

This equation is of interest in that, having all the constants (except η_0) theoretically determined independently of any observations, it does succeed in forecasting observations fairly well between 3 and 15 per cent d.r.c. (Fig. 1). Above this it may be supposed that the missing terms with higher powers of φ become important. It would be of theoretical interest to more thoroughly investigate conditions in the region of 0 to 3 per cent d.r.c.

Bächle (1936) compared his observations on latex with Guth's equation; but instead of φ he used $\varphi(1-\varphi)$, *i.e.* the ratio of disperse phase: serum*. With this modification he claimed that the equation gave a faultless ("*tadellose*") agreement with his observations up to 45 per cent d.r.c. The equation fits our data equally well (but not faultlessly) up to 30 per cent d.r.c., φ being estimated as above (Fig. 2).†

Now Guth (p. 155) states that, when the corrections are larger than the basic value indicated by Einstein's equation, their construction by means of a power series is no longer permissible. In these circumstances he recommends that his equations should

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* This is not indicated in the text of Bächle's paper, but has been pointed out to us in correspondence.

† Bachle has not published his data and the scales attached to his graph are not indicated with sufficient accuracy to enable us to make detailed comparison between his results and ours. The apparent difference in the range of agreement with his theoretical curve could be accounted for, without any appreciable difference in the observations, if in drawing his theoretical curve he used simply d.r.c. by weight in place of φ. War interrupted our correspondence before such points could be elucidated.

be used as giving no more than mere indications of the numerical values to be expected. (He also suggested that they might be used as interpolation formulae, but being both complicated and inflexible they seem to us to be inefficient for this purpose.) Furthermore he considers that the superficial analogy to van der Waals' equation, by which some previous workers have replaced φ in Einstein's equation by $\varphi/(1-\varphi)$, or by $\varphi/(1-k\varphi)$*, is not permissible; and he apparently intends that the expansion in powers of φ which he has proposed should replace this. Therefore when Bächle inserts $\varphi/(1-\varphi)$ in Guth's equation he would appear to be confusing ideas which were intended to be separate. Nevertheless the success of Bächle's equation suggests that it might deserve consideration by someone who is more competent than are we to investigate the theoretical background. Meantime, since independent justification appears at present to be lacking, it cannot be interpreted (as in Bächle's paper) "in support of the accuracy of measurements by the Höppler viscometer."

Whatever may be the theoretical interest of Bächle's equation, it is not suitable for use as a statistical tool to investigate variations which occur in practice: not only because it fails to describe observed viscosities over a sufficiently wide range; but also because, being inflexible in form, it cannot be fitted to different groups of data, to estimate average values, and to investigate differences between groups of latices.

For emulsoid sols in which the disperse phase consists of elastically deformable particles occupying more than one-half of the total volume Hatschek (1911) deduced a formula based on geometrical considerations, *viz.*

$$\eta = \frac{\eta_0}{1 - \sqrt[3]{(hw)}}$$

where h is intended to be a hydration factor combined with the reciprocal of the specific gravity of the disperse phase, so that hw represents the volume of disperse phase, including water of hydration, in unit volume of the sol. He has applied this formula to estimate hypothetical values of h at varying concentrations.

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* If, as used above, φ represents the volume concentration of dry rubber, the constant k might be taken to be an estimate of increase in the volume of disperse phase due to water of hydration and other adsorbed substances. The introduction of k into Bächle's equation is however of no help in adjusting this equation to latex data. Fitting

$$\eta = \eta_0 \, [1 + 2.5 \, \varphi/(1 - k\varphi) + 7.79 \, \varphi^2/(1 - k\varphi)^2]$$

to the data of series 3 by the method of least squares, we obtain $\log_{10}\eta_0 = -0.057$, $k = 1.29$. This gives a curve which starts below the observations ($\eta_0 = 0.88$, instead of 1.06), crosses them at 26 per cent d.r.c., and continues above them to the highest observation at 66 per cent d.r.c.: a curve which is of no interest whatsoever and merely shows the inability of the equation to fit the data over their whole range.

Applying this procedure to mean viscosities for the four mixture series we find:

w	...	0.02	0.30	0.37	0.52	0.56	0.66
h	...	0.011	1.09	1.34	1.58	1.58	1.48
hw	...	—	<.5	0.50	0.82	0.88	0.98

Since, with increasing concentration, water of hydration, and therefore h, should either remain constant or decrease, it does not appear that this formula can have any meaning for latex of less than 52 per cent d.r.c.

Arrhenius (1916) also has introduced the idea of hydration into his logarithmic formula, *viz.*

$$\log \eta/\eta_0 = \frac{K w}{1-(n+1) w}$$

where n is supposed to represent water of hydration. This formula fits the observations on latex very well, but since the regression of log η on $w(1-w)$is concave downward (Fig. 3), n must be negative. Therefore the formula can have no theoretical validity; and although it might serve very well as an empirical equation, more satisfactory ones can be devised.

In view of these comparisons of the viscosity of latex with the equations of Guth, Hatschek and Arrhenius, and of the close agreement of results obtained with two different viscometers, it might be tentatively suggested that latex seems to behave in these experiments as a hydrophobic sol. Obviously however no firm conclusion can be drawn on this evidence.

With no regard to theoretical considerations a large number of formulae can be devised to describe the observations empirically. Of those which have occurred to us we have selected two for detailed considerations, *viz.*

$$\log (\eta + a) = b + cr \qquad \text{(I)}$$

$$\log \eta = a^1 + b^1 \tan p \qquad \text{(II)}$$

where r = ratio of rubber to serum = $w/(1-w)$, w being, as above, weight concentration, or d.r.c. per cent ÷ 100, p = d.r.c. per cent represented as an angle in degrees, and a, b and c are arbitrary constants (of which $a^1 = \log \eta_0$).

Equation (I) seems the more natural since it has a fairly simple meaning. It indicates an approximately linear relationship between log η and r when η is large relative to a, *i.e.* it indicates that relative changes in viscosity are approximately proportional to the ratio of rubber: serum. The constant a may be regarded as a correction factor for low concentrations. The equation is, for empirical purposes, similar to Arrhenius' equation, except that the adjustment for curvature of the regression of log η on r has been introduced at a different place. It seems however to be preferable to Arrhenius' equation because, the idea of hydration underlying

Arrhenius' formula having been abandoned, equation (I) is simpler in form and shows more clearly the interpretation just given. Furthermore it seems to give a slightly truer description of the data. Arrhenius' equation fails to curve downward sufficiently near zero d.r.c. and is too low at the highest concentrations.

For statistical purposes however equation (I) is not very convenient as it gives η only as an implicit function of r and cannot be readily fitted to any given set of data. Equation (II), on the other hand, being a simple linear equation between two tabulated functions, is ideal, both for statistical comparisons and as a simple formula to estimate viscosity of latex for any given d.r.c.

Both equations fit the data equally well. When they are fitted to the combined data of the four mixture series, and of the commercial samples (Höppler groups), allowance being made for differences between means of series but not for differences in slope, the mean variances of deviations of log η from the regressions are

	Mixtures	Commercial
from equation (I): -	0.573×10^{-3}	0.221×10^{-3}
„ „ (II): -	0.523×10^{-3}	0.216×10^{-3}

The seven series of data have been compared by fitting equation (II) to each separately. They show small differences both in slope (b^1) and in the mean viscosities for any given d.r.c. Possible causes of these differences may be source of latex, time of tapping, treatment of latex, or differences in the technique of testing such as variation in the temperature between 28 and 30° C. The results will not however be set forth in detail because from information now available it is not possible to disentangle the effects of these factors. As may be seen from the figures the chief difference was that the serum-concentrate Series 1 and 2 and the skim-cream series (all from the same estate), and the Dunlop concentrate group, showed lower viscosities than Series 3 and the samples of field latex. The difference in log η was of the order of .05, *i.e.* differences in absolute viscosity were about 12 per cent.

The best fitting regressions for the combined data of the four series of mixtures are (Figs. 3 and 5).

$$\log (\eta + 0.309) = 0.143 + 1.014\, r \qquad (1)$$

$$\log \eta = 0.010 + 0.942 \tan p \qquad (2)$$

η being measured in centipoises, and logarithms being to the base 10.

In estimating a mean regression for the samples of field latex it must be borne in mind that the data are somewhat heterogeneous and owing to the loss of the detailed data we cannot now

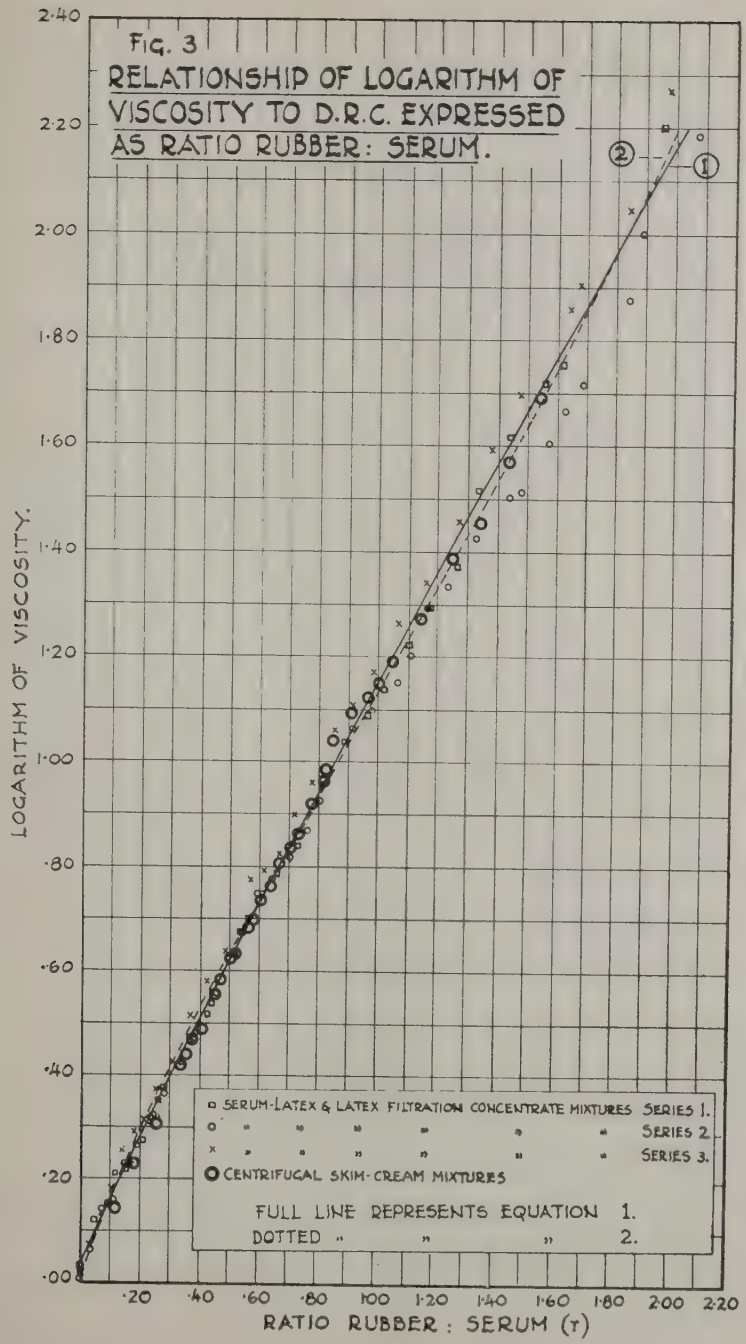
Fig. 3
RELATIONSHIP OF LOGARITHM OF VISCOSITY TO D.R.C. EXPRESSED AS RATIO RUBBER: SERUM.
2·40
2·20
2·00
1·80
1·60
1·40
1·20
1·00
·80
·60
·40
·20
·00
LOGARITHM OF VISCOSITY.
·20 ·40 ·60 ·80 1·00 1·20 1·40 1·60 1·80 2·00 2·20
RATIO RUBBER : SERUM (r)
② ①
□ SERUM-LATEX & LATEX FILTRATION CONCENTRATE MIXTURES SERIES 1.
○ " " " " " " SERIES 2.
× " " " " " " SERIES 3.
◎ CENTRIFUGAL SKIM-CREAM MIXTURES
FULL LINE REPRESENTS EQUATION 1.
DOTTED " " " 2.

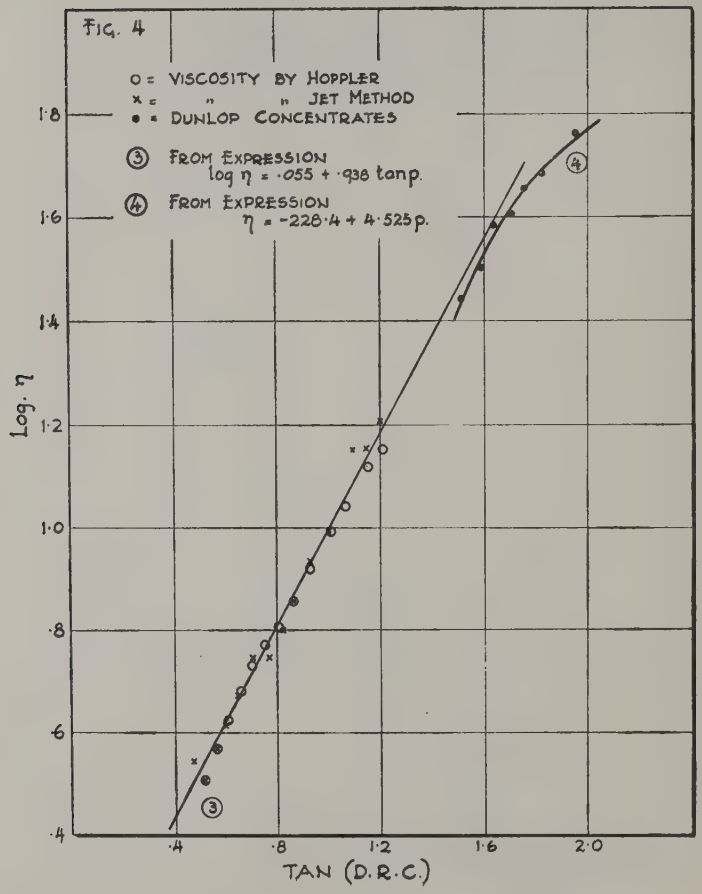
FIG. 4
o = VISCOSITY BY HOPPLER
x = " " JET METHOD
• = DUNLOP CONCENTRATES
③ FROM EXPRESSION
log η = ·055 + ·938 tanp.
④ FROM EXPRESSION
η = -228·4 + 4·525p.
Log. η
1·8
1·6
1·4
1·2
1·0
·8
·6
·4
·4
·8
1·2
1·6
2·0
TAN (D.R.C.)

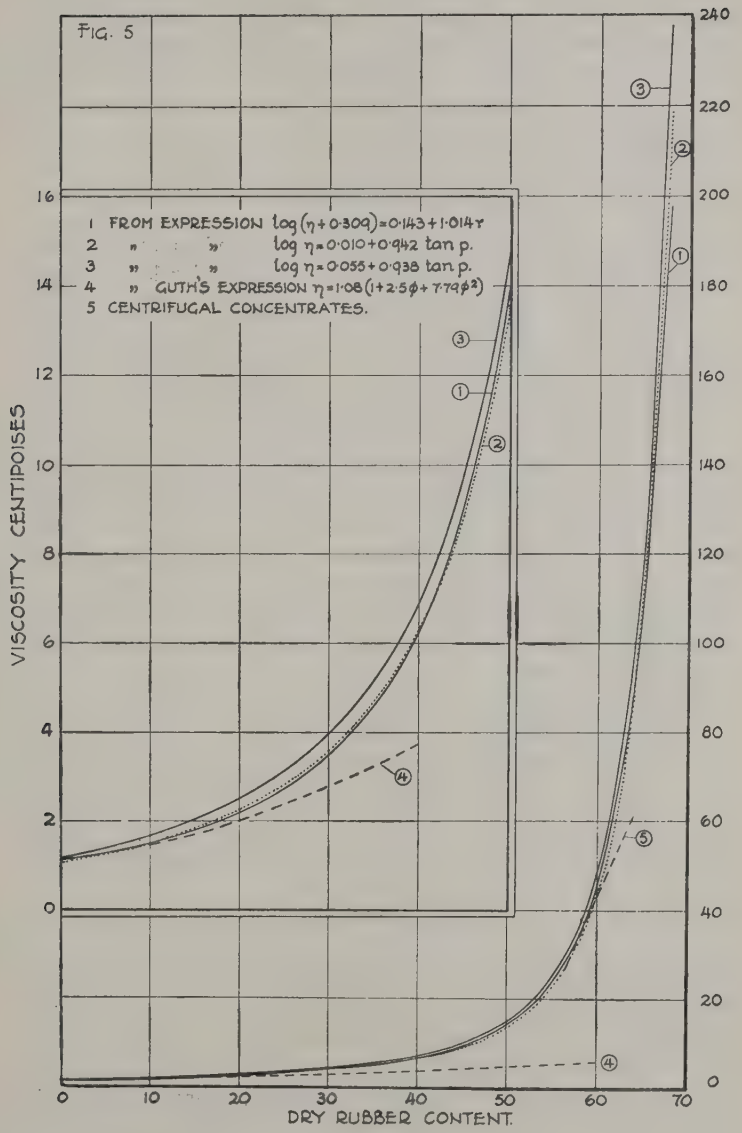
FIG. 5
1 FROM EXPRESSION log (η + 0·309) = 0·143 + 1·014τ
2 " " log η = 0·010 + 0·942 tan p.
3 " " log η = 0·055 + 0·938 tan p.
4 " GUTH'S EXPRESSION η = 1·08 (1 + 2·5φ + 7·79φ²)
5 CENTRIFUGAL CONCENTRATES.
VISCOSITY CENTIPOISES
DRY RUBBER CONTENT.
0
2
4
6
8
10
12
14
16
0
20
40
60
80
100
120
140
160
180
200
220
240
0
10
20
30
40
50
60
70

sort it out into groups representing different sources, times of tapping etc. In particular it is known that the majority of the samples with low d.r.c. came from a division of one estate (Kepong) on which mild slaughter-tapping was being carried out. There is therefore reason to suppose that values of η below expectation in the lowest d.r.c. classes may be owing to some special character of latex from this source and may not represent the normal relationship between viscosity and d.r.c. in this region.

Now equation (I) is sensitive to curvature in this region. If it be fitted to these data and extrapolated to $r = 0$ it gives $\eta_0 = .83$ which is too low, thereby tending to confirm our suspicion that the apparent curvature shown by the data for low values of d.r.c. may be an artifact. Equation (II), on the other hand, is not susceptible to this curvature. Therefore for the purpose of estimating the average results for field latex it seems preferable to use only Equation (II) and to ignore Equation (I).

Further when pooling the data of Table I it may be noted that the Höppler viscometer would be expected to give more accurate observations than could be obtained with the older and somewhat "home-made" pipette apparatus, which tended to show some irregularity at viscosities between 5 and 7 centipoises. Regressions fitted to each group separately showed variances about regressions of 0.162×10^{-3} and 0.293×10^{-3} for the Höppler and pipette groups respectively. Therefore to obtain an average regression for both groups the pipette data have been weighted by 0.55 (= 0.162/.293).

The mean regression for the two groups is, (Fig. 4),

$$\log \eta = 0.055 + 0.938 \tan p \qquad (3)$$

The viscosities of the samples of centrifugal concentrates fall significantly below the values indicated by extrapolating equation (3) (Fig. 4). Furthermore the observations do not conform to a linear relationship of $\log \eta$ on either r or $\tan p$. In fact the linear relationship appears to be between the primary variates, η and d.r.c., *viz.*

$$\eta = -228.4 + 4.525\, p \qquad (4)$$

Obviously this relationship must be artificial and cannot be extrapolated outside the observed range.

The general relationship between η and d.r.c. per cent is shown graphically in Fig. 5, where equations (1), (2), (3) and Guth's formula are compared.*

Table IV, based on equations (3) and (4) may be used for reference to indicate the viscosity at 30° C. of average ammoniated latex of any dry-rubber-content. In so far as our samples may

* For graphs showing original data plotted on the scales of centipoises: d.r.c. per cent, see *India Rubber Journ. loc. cit.*

be representative of commercial samples at large, they indicate that individual samples may vary about the figures in Table IVa (field latex) with a standard deviation of 3.5 per cent (or 3.0 per cent for Höppler observations only), and about the figures in Table IVb (Dunlop centrifugal concentrates) with a standard deviation of 0.74 centipoise.

TABLE IV

Viscosity Table for Latex and Latex Concentrates

(Viscosity in centipoises at 30° c)

(a) *for ammoniated field latex**

d.r.c. per cent	0	2	4	6	8
20	2.49	2.72	2.97	3.26	3.58
30	3.95	4.38	4.87	5.45	6.14
40	6.95	7.94	9.14	10.62	12.50
50	14.89	18.01	22.18	27.90	35.98
60	47.83	65.94	95.10	145.14	238.03

Note: This table is to be read like a log table, *e.g.* the viscosity for latex of 34 per cent d.r.c. = 4.87 cp.

(b) *for centrifugal concentrates (Dunlop)*†

d.r.c.	56	58	60	62	64
η	25.0	34.0	43.1	52.1	61.2

* Calculated from equation (3)

$$\log \eta = 0.055 + 0.938 \tan p$$

† Calculated from equation (4)

$$\eta = -228.4 + 4.525\ p.$$

Acknowledgements

The authors' thanks are due to Mr. K. C. Sekar and Che Abdul Wahid bin Abdul Wahab for much assistance in the experimental work, and to Mr. Ong Yoke Fong for assistance in the computations.

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*Since these papers are not available in Malaya references to them in this paper are based on reports in textbooks such as those by Bingham, Hatschek, Alexander, etc.

THE VISCOSITY OF PRESERVED AND CONCENTRATED LATEX*

PART II

VISCOSITY—TEMPERATURE RELATIONSHIP OF LATEX

BY

EDGAR RHODES

Summary

The viscosity temperature relationships for normal preserved latex, centrifugal concentrate, and aqueous dilutions of such concentrates, have been determined on a few samples. The results obtained suggest a basis for the calculation of approximate comparative viscosities for normal preserved latex and centrifugal concentrate at different temperatures.

From the viscosity curves for rising and falling temperatures on normal preserved latex and centrifugal concerntrate it appears that normal latex can be heated for several hours at 80° C. without seriously affecting the state of dispersion. There are indications, however, that with rich concentrates heating does affect the state of dispersion slightly.

Introduction

Published data on the viscosity-temperature relationship of latex are very sparse. Bachle (1) made viscosity measurements on 35 per cent and 60 per cent latices between the temperatures of 15° C. and 70° C., and concluded that in both cases the viscosity changes by from 2 to 3 per cent for each degree of temperature change.†

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* This paper is substantially the same as that published, under the same title in *The India Rubber Journal* **97** (1939) 51.

† Readers of the English text of Bächle's paper should note that the curve for 35 per cent latex was obtained by plotting 10 times the observed values. The note indicating this in the original paper (*Kautschuk* **12** 211) has been omitted from the English translation.

Further data on this relationship are now presented, together with the results of some preliminary experiments, which aimed at using viscosity as a means of detecting whether or not the state of the dispersion is changed fundamentally when latex is heated.

Experimental

All the measurements recorded in this paper were made with the Höppler Viscosimeter and the Höppler Ultrathermostat. For the temperature zone 15°-30° C., all determinations were made inside a large refrigerator; the viscosimeter and thermostat were placed bodily inside, and observations were made through specially fitted glass doors.

Observations were, in most cases, made at intervals of 5° C. between the temperatures of 15° and 80° C.

All the latex used in the experiments contained 0.5 per cent ammonia approximately.

The first trials were made with two different samples of centrifugal concentrate. In each case the original concentrate and a series of aqueous dilutions from it were tested over the full temperature range above. Figures 5 and 6 show graphically the results obtained, and Table I gives the experimental data from which the graphs were constructed.

Further trials were also made with normal preserved latex and with a third sample of centrifugal concentrate. In each of these cases the latex was tested at intervals with temperature rising, and then also at intervals on cooling. In one case the latex was allowed to cool steadily, as soon as the viscosity had been recorded at the highest temperature (80° C.), and in the other the latex was held at 80° C. for several hours before being allowed to cool. Further reference is made to this work later in this paper.

Discussion

Viscosity-Temperature

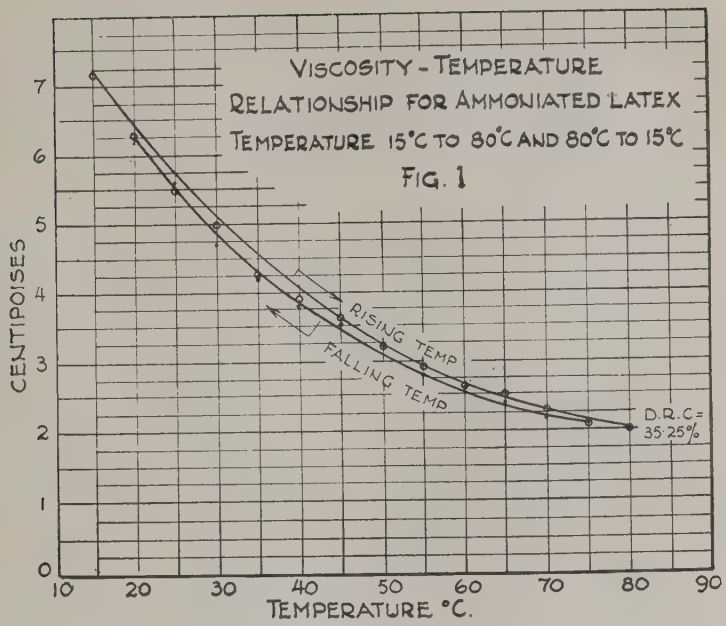
It will be observed from all the figures, and in particular from Figures 5 and 6, that a sharp fall in viscosity results from heating latex above 15° C. At higher temperatures, in the neighbourhood of 60° C., the fall is less pronounced, and the viscosity-temperature curves tend to flatten out. Over the range 15°-80° C. the total fall in viscosity is, in all cases, of the order of 70 per cent of the value at 15° C. With concentrated latex, (Figures 5 and 6,) the fall is much steeper between 15° C. and 20° C. than is the case with normal preserved latex (Figures 1, 2 and 3). The curves for similar samples are of the same shape but not identical.

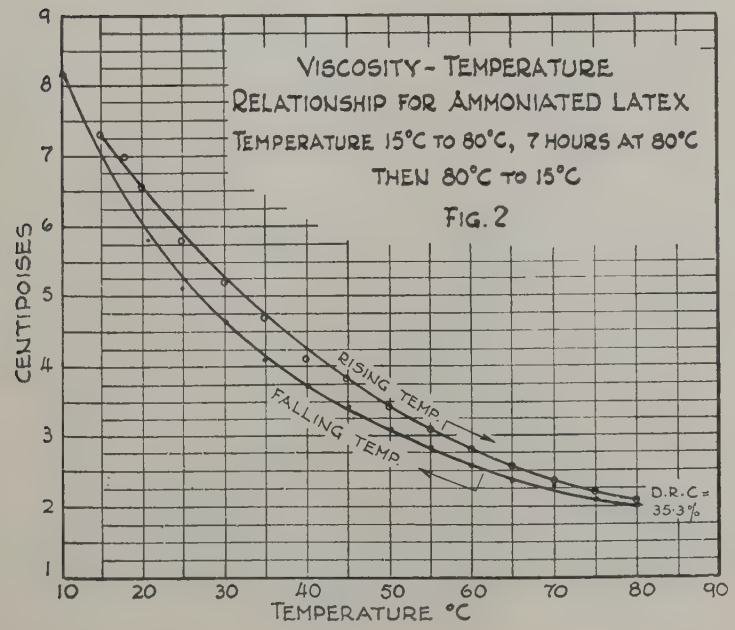
TABLE II

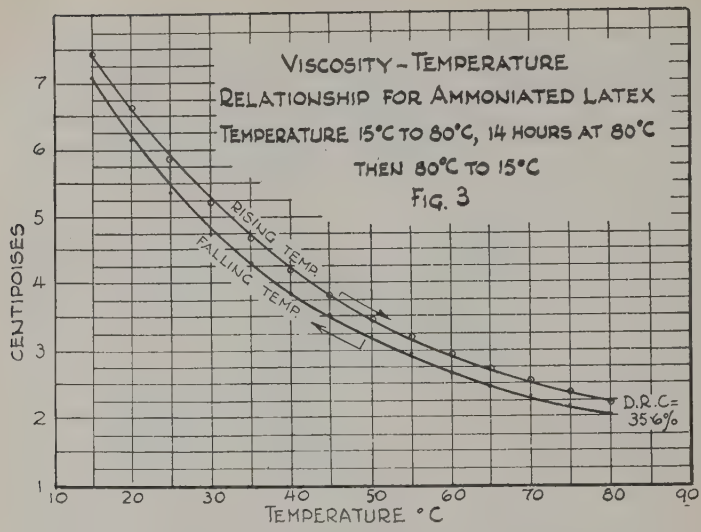
SECTION 1

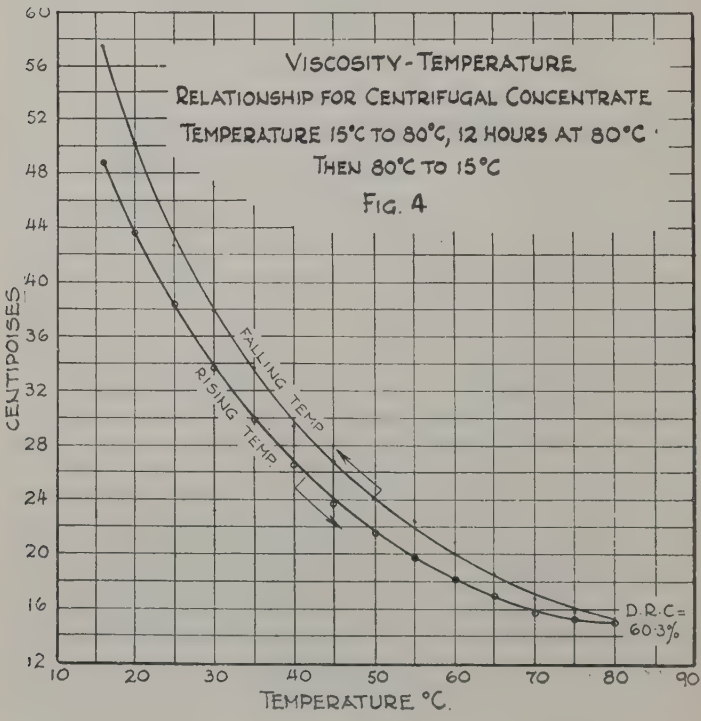
Viscosity (centipoises)															Fall i P	
° C			Zone 15°—50° C					Zone 15°—60° C			Zone 15°—80° C					
15° / 39°	15° / 40.5°	15° / 50°	16° / 50°	17° / 50°	15° / 49°	15° / 50.5°	15° / 60°	16° / 60°	17° / 60°	15° / 80°	16° / 80°	17° / 80°	15° / 75°	15—20 °C	15—3 °C
—	—	4.0	—	—	—	—	4.5	—	—	5.2	—	—	—	2.50	2.04
—	—	3.9	—	—	—	—	4.5	—	—	5.2	—	—	—	1.91	1.92
—	—	4.0	—	—	—	—	4.5	—	—	5.3	—	—	—	2.18	1.81
—	—	—	27.2	—	—	—	—	30.5	—	—	33.9	—	—	2.56	2.20
—	40.2	45.7	—	—	—	—	49.8	—	—	52.7	—	—	—	3.79	3.09
—	—	—	—	36.5	—	—	—	—	41.4	—	—	43.4	—	4.99	2.81
—	—	19.4	—	—	—	—	22.3	—	—	23.4	—	—	—	3.34	2.52
—	—	—	14.1	—	—	—	—	15.0	—	—	17.9	—	—	3.06	2.16
—	—	8.6	—	—	—	—	9.6	—	—	11.0	—	—	—	2.51	2.11
—	—	7.7	—	—	—	—	8.5	—	—	9.7	—	—	—	2.21	1.93
4.6	—	—	—	—	5.7	—	6.6	—	—	7.5	—	—	—	2.80	2.14
—	—	4.6	—	—	—	—	5.2	—	—	—	—	—	5.9	2.27	1.97
—	—	—	—	—	3.7	—	4.1	—	—	5.8	—	—	—	2.00	2.09
—	—	3.0	—	—	—	—	3.5	—	—	4.1	—	—	—	1.64	1.86
—	—	2.9	—	—	—	—	3.3	—	—	3.8	—	—	—	2.72	2.06
—	2.0	—	—	—	—	2.5	2.8	—	—	3.3	—	—	—	2.08	2.08
—	—	2.3	—	—	—	—	2.6	—	—	3.1	—	—	—	2.17	1.88
—	—	1.7	—	—	—	—	2.1	—	—	2.5	—	—	—	2.02	1.80

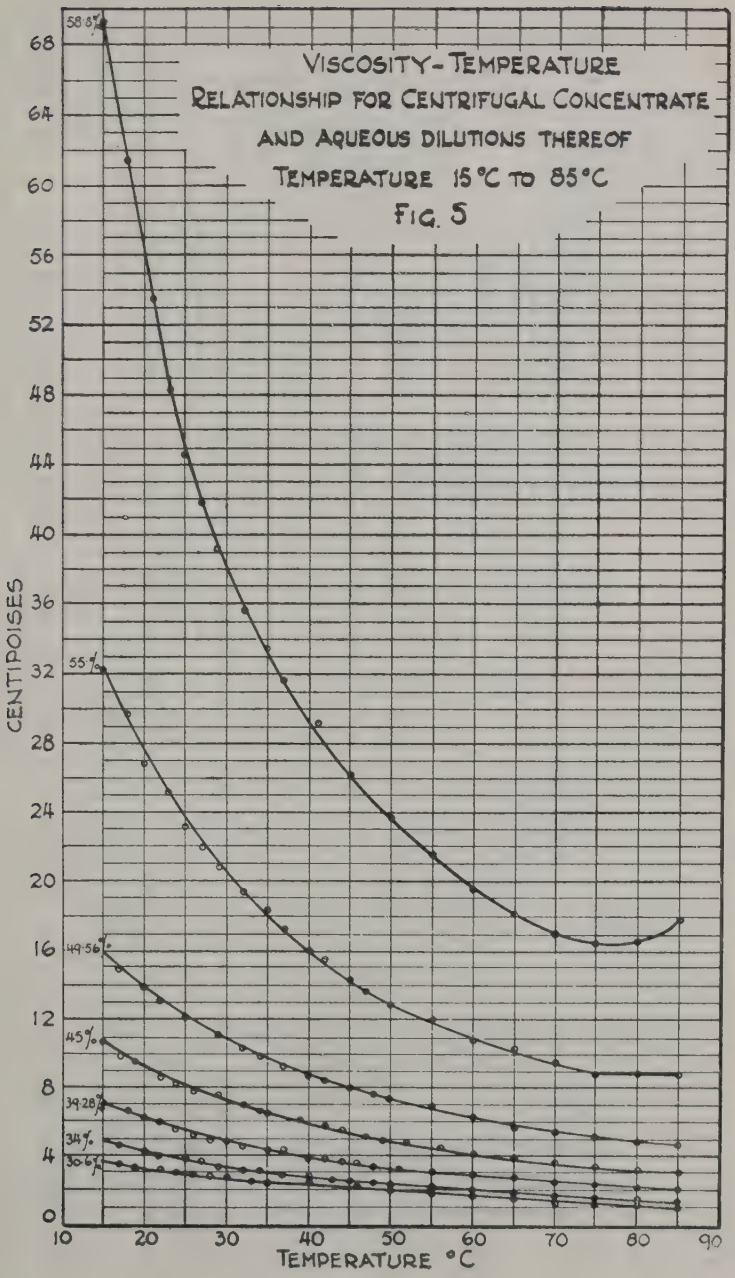
ECTION 2				SECTION 3					
scosity from initial ent. per degree				Fall in viscosity from initial Per cent. per degree					
Zone				Zone mean					
—40 °C	15—50 °C	15—60 °C	15—80 °C	15—20 °C	15—30 °C	15—40 °C	15—50 °C	15—60 °C	15—80 °C
1.83	1.59	1.39	1.11						
1.75	1.53	1.37	1.09	2.20	1.92	1.78	1.55	1.37	1.10
1.77	1.53	1.34	1.09						
1.89	1.64	1.42	1.08						
2.27	1.88	1.59	1.17	3.78	2.70	2.10	1.77	1.53	1.12
2.15	1.80	1.57	1.12						
2.01	1.71	1.53	1.11						
1.83	1.59	1.31	1.07						
1.79	1.55	1.34	1.08	2.70	2.14	1.81	1.57	1.36	1.08
1.74	1.52	1.30	1.03						
1.79	1.57	1.37	1.08						
1.68	1.49	1.31	1.12						
1.77	1.55	1.30	1.27						
1.64	1.40	1.27	1.03						
1.74	1.51	1.33	1.06	2.11	1.96	1.64	1.45	1.29	1.08
1.63	1.47	1.30	1.06						
1.65	1.43	1.25	1.04						
1.41	1.31	1.26	1.04						

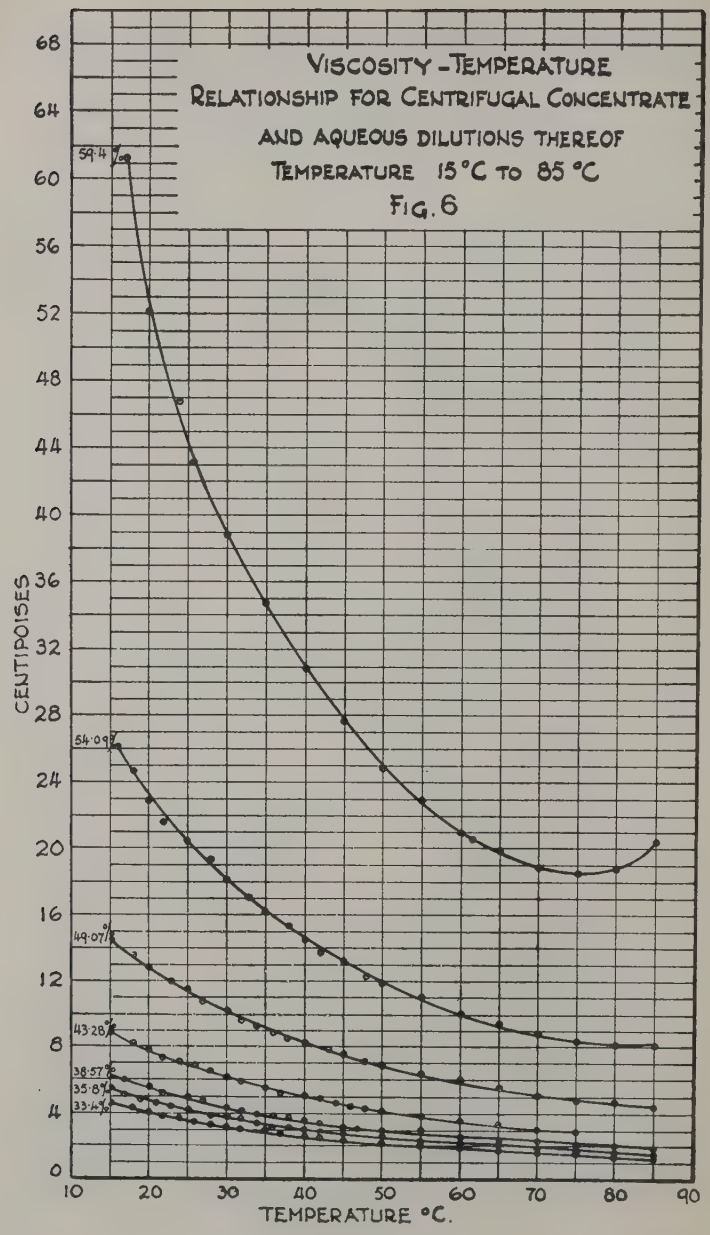

VISCOSITY - TEMPERATURE
RELATIONSHIP FOR AMMONIATED LATEX
TEMPERATURE 15°C TO 80°C AND 80°C TO 15°C
FIG. 1
CENTIPOISES
TEMPERATURE °C.
RISING TEMP
FALLING TEMP
D.R.C = 35·25%


VISCOSITY - TEMPERATURE
RELATIONSHIP FOR AMMONIATED LATEX
TEMPERATURE 15°C TO 80°C, 7 HOURS AT 80°C
THEN 80°C TO 15°C
FIG. 2
CENTIPOISES
TEMPERATURE °C
RISING TEMP
FALLING TEMP
D.R.C = 35·3%


VISCOSITY-TEMPERATURE
RELATIONSHIP FOR AMMONIATED LATEX
TEMPERATURE 15°C TO 80°C, 14 HOURS AT 80°C
THEN 80°C TO 15°C
FIG. 3
CENTIPOISES
TEMPERATURE °C
RISING TEMP.
FALLING TEMP.
D.R.C= 35·6%


VISCOSITY-TEMPERATURE
RELATIONSHIP FOR CENTRIFUGAL CONCENTRATE
TEMPERATURE 15°C TO 80°C, 12 HOURS AT 80°C
THEN 80°C TO 15°C
FIG. 4
CENTIPOISES
TEMPERATURE °C.
FALLING TEMP.
RISING TEMP.
D.R.C= 60·3%


VISCOSITY-TEMPERATURE
RELATIONSHIP FOR CENTRIFUGAL CONCENTRATE
AND AQUEOUS DILUTIONS THEREOF
TEMPERATURE 15 °C TO 85 °C
FIG. 5
CENTIPOISES
TEMPERATURE °C
58·8%
55%
49·56%
45%
39·28%
34%
30·6%
0
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
64
68
10
20
30
40
50
60
70
80
90


VISCOSITY - TEMPERATURE
RELATIONSHIP FOR CENTRIFUGAL CONCENTRATE
AND AQUEOUS DILUTIONS THEREOF
TEMPERATURE 15°C TO 85°C
FIG. 6
CENTIPOISES
TEMPERATURE °C.
54·4%
54·09%
49·07%
43·26%
38·57%
35·8%
33·4%
0
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
64
68
10
20
30
40
50
60
70
80
90

In order to arrive at an estimate of the rate at which viscosity decreases with rising temperature, Table II, derived from Table I, was prepared. This shows:—

(i) The actual fall of viscosity in centipoises over various temperature zones for all the specimens examined.

(ii) The fall in viscosity per cent. per degree, from the initial viscosity at *circa* 15° C. These figures are derived from those in Section (i) of Table II above.

(iii) The mean fall in viscosity per cent. per degree for the various zones, for latices of similar kinds, namely:—

(*a*) Normal preserved latex.

(*b*) Centrifugal concentrates.

(*c*) Dilutions from centrifugal concentrates of higher dry-rubber-content than commercial preserved normal latex, *i.e.*, higher than 40 per cent dry-rubber-content.

(*d*) Dilutions from centrifugal concentrate of dry-rubber-content less than 40 per cent.

These values arise from Section (2) of Table II.

From a study of Table II it may be seen that the various types of latex do not respond identically to increasing temperature, the latices of high dry-rubber-content showing a much more rapid fall in viscosity in the initial stages of heating. This rapid fall is not maintained, however, and it is seen from Table II, Sections 2 and 3, that over the whole range of 15°-80° C. the mean percentage fall in viscosity per degree is, within very small limits, the same for all the types of latex examined, namely, of the order of 1.1 per cent per degree Centrigrade. This figure is approximately half that found by Bachle (*loc. cit.*). It will be observed from Table II, Section 3, that the low d.r.c. group of dilutions from centrifugal concentrate respond to heat in a manner very similar to the normal preserved latices, while the richer group show, in the early stages, values intermediate between the normal latex and the centrifugal concentrates.

It is not possible from the meagre data at present available to predict accurately the corrections which should be made for different temperatures, but from a consideration of Table II, Section 3, it is suggested that for approximate use the following values should be taken:—

TABLE III

Type of Latex	Fall in Viscosity from Value at 15° C. (per cent. per degree)					
	Zone					
	15—20 °C.	15—30 °C.	15—40 °C.	15—50 °C.	15—60 °C.	15—80 °C.
Normal preserved ...	2.2	2.0	1.7	1.5	1.3	1.1
Centrifugal concentrate ...	3.8	2.7	2.1	1.8	1.5	1.1

On this basis a rough table for the comparative viscosities of commercial preserved latex and centrifugal concentrate can be drawn up for any desired temperature zone. The values for the temperatures 15° C., 20° C., and 30° C. which are the most likely to be required are:—

TABLE IV

Comparative Viscosities at Different Temperatures

Type of Latex	Viscosity (centipoises)		
	15° C.	20° C.	30° C.
	5.0	4.5	3.5
Preserved Latex	6.0	5.4	4.2
	7.0	6.3	5.0
Zone 30—40 per cent. approx.	8.0	7.1	5.7
	9.0	8.1	6.4
	10.0	8.9	7.1
	45.0	36.5	26.4
	50.0	40.5	29.8
	55.0	44.5	32.7
Centrifugal Concentrate	60.0	48.6	35.7
	65.0	52.7	38.7
Zone 56—61 per cent. approx.	70.0	56.7	41.7
	75.0	60.8	44.6
	80.0	64.8	47.6
	85.0	68.9	50.6
	90.0	72.9	53.6

Similar tables for other zones can be constructed at will from the values in Table III.

Viscosity Hysteresis

It will have been observed from Figures 5 and 6 that the viscosity curves for the undiluted concentrates have a slight upward trend between the temperatures of 75 and 85° C. This would seem to indicate that on heating to these high temperatures a change in the state of the latex dispersion begins to take place. If the change is a real one, then on heating latex to a high temperature and later allowing it to cool, the viscosity curve for falling temperature should show appreciable departure from the curve for rising temperature.

A few trials were accordingly made with fresh ammoniated latex and freshly prepared centrifugal concentrate. The experimental results obtained are set out in Table V, and are shown graphically in Figures 1 to 4 inclusive.

It will be observed from Figure 1 that when freshly prepared normal preserved latex is heated to 80° C. and allowed to cool, the viscosity curves for rising and falling temperature lie very close to each other. The degree of hysteresis is negligible. This would indicate that the state of the dispersion has not been changed materially.

When similar freshly preserved latex is heated to 80° C., and held at this temperature for periods of 7 and 14 hours respectively (see Figures 2 and 3), the cooling curves lie below and run almost parallel with the heating curve, indicating that the heating has brought about a slight but permanent reduction in viscosity. The inference is that under the prolonged heating at 80°C. some non-rubber bodies, which contributed slightly to the viscosity, have been in part hydrolyzed by the ammonia to less viscous substances. Because the heating and cooling curves are so close together, and so similar with the cooling curve below the heating curve, it seems safe to assume that the heating has not changed fundamentally the state of the dispersion.

When centrifugal concentrate is heated to 80° C., and held there for 12 hours before cooling, the results are somewhat different. The cooling curve now lies above the heating curve. At 80° C. the viscosity, after 12 hours' heating, is not far removed from that recorded before the heating, but, as cooling proceeds, the heated latex becomes notably more viscous; at 15° C. the difference in viscosity of the heated and unheated latex is nearly 9 centipoises. It would appear that with rich latex, prolonged heating at 80° C. affects slightly the state of the dispersion. This result is in line with the inference drawn from the curves in Figures 5 and 6.

TABLE V

Viscosity Hysteresis on Heating and Cooling

Sample	Type of Latex	DRC (per cent)	Period held at 80° C after initial determination at 80° C (hours)	Rising or Falling	VISCOSITY (centipoises) TEMPERATURE °C																								
					10	15	16	18	20	20.5	21	25	25.5	30	30.5	35	35.5	40	45	45.5	50	55	60	65	65.5	70	75	80
Fig. 1	Normal preserved	35.25	nil	Rising	—	7.2	—	—	6.3	—	—	5.5	—	5.0	—	—	4.3	3.9	3.6	—	3.2	2.9	2.7	2.5	—	2.3	2.1	2.0
				Falling	—	—	—	—	—	6.2	—	—	5.6	—	4.7	—	4.2	3.8	—	3.5	3.2	2.8	2.6	—	2.4	2.2	2.1	—
Fig. 2	Normal preserved	35.3	7	Rising	—	7.3	—	7.0	6.6	—	—	5.8	—	5.2	—	4.7	—	4.1	3.8	—	3.4	3.1	2.8	2.6	—	2.4	2.2	2.1
				Falling	8.2	—	—	—	—	—	5.8	5.1	—	4.6	—	4.1	—	3.7	3.4	—	3.1	2.8	2.6	2.4	—	2.3	2.1	2.0
Fig. 3	Normal preserved	35.6	14	Rising	—	7.5	—	—	6.6	—	—	5.9	—	5.2	—	4.7	—	4.2	3.8	—	3.5	3.2	3.0	2.7	—	2.5	2.4	2.2
				Falling	—	7.1	—	—	6.1	—	—	5.3	—	4.8	—	4.3	—	3.8	3.5	—	3.2	3.0	2.7	2.5	—	2.3	2.2	2.0
Fig. 4	Centrifugal Concentrate	60.3	12	Rising	—	—	48.8	—	43.8	—	—	38.4	—	33.8	—	29.9	—	26.6	23.8	—	21.6	19.8	18.3	17.1	—	15.8	15.3	14.9
				Falling	—	—	57.5	—	50.3	—	—	42.8	—	37.9	—	33.6	—	29.4	26.7	—	24.1	22.4	20.9	18.6	—	16.9	15.8	15.3

Acknowledgments

The author's thanks are due to Mr. K. C. Sekar and Che Abdul Wahid bin Abdul Wahab for assistance in carrying out the viscosity determinations.

Reference

1. O. Bachlé. *Rub. Chem. & Tech.*, **10** (1937) 675-681